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ON THE ACTION
OF
NITRIC AND NITROUS ACIDS
ON
THE SULPHOCYANIDES.

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SOME time since, having had occasion to test a sample of carbonate of potash (which I believed to be very pure), to ascertain if it was perfectly free from iron, and suitable for the purpose required, I was surprised, on dissolving a little of it in water and supersaturating the solution with some carefully purified nitric acid, to find that the mixture, on the addition of a few drops of a solution of sulphocyanide of potassium, became of a reddish colour, indicating apparently the existence of a small quantity of iron in the mixture. Conceiving that the coloration observed was caused by the presence of that metal, I proceeded to ascertain whether it existed in the acid or in the carbonate. A few experiments showed me that the effect was due to the acid; for I found, on testing a diluted portion of it with sulphocyanide of potassium, that it soon acquired the same reddish tint; whereas some of the carbonate of potash, after supersaturation with pure hydrochloric acid, did not acquire the reddish tinge on the addition of the sulphocyanide, or give the slightest indication of iron when tested with either the ferrocyanide or ferridcyanide of potassium, clearly proving that the effect observed was alone attributable to the acid. This I thought was rather singular, as the nitric acid I employed was very carefully prepared by myself, and I believed that it was chemically pure. A considerable portion, however, of this acid being evaporated down to dryness in a porcelain dish on a water-bath, and some pure hydrochloric acid added to the minute residue which remained, and the evaporation repeated to destroy any nitric acid existing in it, I found that this residue, being dissolved in water, gave, both with the sulphocyanide and ferrocyanide of potassium, indications of the presence of a very minute quantity of iron, which I conceived was not at all sufficient to account for the former very decided effects I had observed in treating the acid with sulphocyanide of potassium.

It thus remaining doubtful whether the effect observed was due to the action of the acid itself on the sulphocyanide or, at least in part, to the trace of iron which was found to exist in it, I very carefully redistilled some of this nitric acid; and having satisfied myself that it was then perfectly free from iron (by testing in the manner just described), I tried its action on the sulphocyanide, when I found that the same reddening effect as in the former case was produced, clearly showing that its production was independent of the presence of iron, and was caused by the action of the acid on this salt.

Not finding, in the chemical works I was able to refer to, any mention made of the development of this red compound under the particular circumstances which I have just described, I proceeded to examine the subject more minutely. I found that on adding a few drops of this pure nitric acid to a solution of the sulphocyanide of potassium the red coloration developed itself, and, having become more and more intense up to a certain point, it gradually disappeared, leaving the mixture perfectly transparent and colourless, the change being generally attended with the evolution of very minute globules of gas. The application of a gentle heat I found very quickly developed the red coloration, and of a much greater degree of intensity than when left to itself, so that the mixture acquired a dark blood-red colour (precisely similar to the sulphocyanide of iron in appearance); but when thus formed it very quickly again disappeared with the copious evolution of gaseous matter, unless the mixture was at once cooled; but even then it only remained a short time longer, becoming, as in the former cases, perfectly colourless. I ascertained also, where the solution of sulphocyanide had been heated with the nitric acid, and after developing the red coloration it had become colourless, that, if the mixture was then cooled to the ordinary temperature, it immediately acquired, on the addition of a few fresh drops of the solution of sulphocyanide, the same intense red colour without the assistance of any heat; and the same I afterwards found to be the case where these substances had more slowly reacted on each other at the ordinary temperature. These observations led me to infer that the coloration was immediately due to the action of nitrous acid, or at least to some lower oxide of nitrogen than nitric acid, produced by the deoxidation of that acid, from its giving oxygen to the constituents of a part of the sulphocyanide, whilst the reduced portion of the acid, reacting on the rest, gave rise to the formation of the red compound. That this inference was correct, appeared to be shown by the immediate and much more striking effect which was produced by a portion of the same pure and colourless nitric acid after it had suffered reduction to some extent by its being made to act on a little alcohol, sugar, or starch, or even by exposure to strong sunlight for a short time before the addition of the sulphocyanide. But what appeared to be still more conclusive as to nitrous acid being the chief agent in the formation of this peculiar red combination were the following facts:—Having prepared nitrite of potash by strongly heating some pure nitre, I found that a little of the salt so obtained, being dissolved in water and mixed with some sulphocyanide of potassium, developed instantly, and without the assistance of heat, an intense blood-red coloration, after the addition of a few drops of pure diluted hydrochloric or sulphuric acid had been added to the mixture to set free the nitrous acid combined with the potash.

That the production of this red compound, under the circumstances described, is not confined to the combination of sulphocyanogen with potassium, was shown by my obtaining it where I employed other sulphocyanides, as those of sodium, ammonium, and silver, as well as with the hydrosulphocyanic acid itself; so that it is probable that it belongs to all the sulphocyanides, which are either soluble, or the sulphocyanogen of which is capable of liberation when acted on in the manner described.

As to the reaction which takes place, or the exact nature of this red compound which is formed when nitrous acid thus acts on the sulphocyanides, it is very difficult to determine, owing chiefly to the great instability of this peculiar compound; for it is no sooner formed than it begins to decompose and disappear, evolving, amongst other gaseous products, the binoxide of nitrogen, which can be easily recognized by the usual tests for that substance; whilst the presence of sulphuric acid can be readily detected in the mixture. But though this part of the subject is surrounded with many difficulties, I purpose continuing its investigation in the hope of throwing some additional light on the nature of this interesting reaction. In the meantime, however, the observations I have made appear to me of sufficient interest and importance to be placed on record as having some practical bearings in an analytical point of view; for many cases may occur in different chemical researches where the production of this peculiar red compound may be mistaken for the presence of iron, as, for example, in testing sulphuric, hydrochloric, or nitric acid for iron, as well as in searching for the same metal in the salts of the alkalies, &c., wherein the sulphocyanide of potassium (one of our most delicate tests for iron) is used, either alone or in conjunction with hydrochloric, sulphuric, or nitric acid, as the means of detecting that metal; for the apparent indications of iron so obtained may be only caused by the action of the nitric or nitrous acid used, or present in the other acids employed, or even by the presence of some nitrates or nitrites in the compounds under examination, the nitrogen acids of which, being set free by the sulphuric or hydrochloric acid employed, reacting on the sulphocyanide, may be the sole cause of the effect which might be so naturally mistaken for iron. I have ascertained, however, that there are several points of distinction between the red compound produced by the action of the nitrogen acids on the sulphocyanides, and the sulphocyanide of iron, resembling it so closely in appearance, which may be easily taken advantage of in distinguishing one from the other. Amongst these the following may be mentioned:—

1st. The former is very unstable, and completely disappears on standing a short time, or immediately on heating it; whereas the latter possesses considerable permanence at the ordinary temperature, and even only very slowly disappears by the continued application of heat.

2nd. The smallest portion of a solution of the ferrocyanide of of potassium added to a mixture coloured red by the sulphocyanide of iron instantly changes its colour to a deep blue; whereas, in the other case, that reagent appears at first to have very little effect on its colour, till it has been added in considerable quantity, when its dark red coloration gradually passes into a bright yellow, owing apparently to the conversion of the ferrocyanide into ferridcyanide of potassium; whilst each drop of the reagent added is attended with the copious evolution of small globules of gas.

3rd. The alkalies (potash, soda, and ammonia) added in excess, decolorize both red compounds; but this in the case of the metal iron is attended with the precipitation of its oxide, whereas there is no precipitation whatever produced with the other compound. On the addition, however, of an excess of either hydrochloric or sulphuric acid the red coloration is restored in both cases. The above differences will easily enable us to distinguish between these two compounds; but, in addition to them, I may mention another interesting peculiarity I have observed in the case of the compound formed by the nitrogen acids and their salts—that it is very quickly taken up and dissolved by chloroform, ether, benzole, or bisulphide of carbon when those liquids are agitated with mixtures containing it, leaving them nearly colourless, whilst those substances themselves acquire an intense blood-red colour, which, however, soon again disappears, evolving globules of gas. Solutions containing the sulphocyanide of iron, on the other hand, when agitated with those liquids, do not impart to them any colour (except in the case of ether, which acquires a very faint pinkish tint), whilst the solutions themselves remain of the same intensity of colour as they possessed before the agitation with those substances. So that in these, and many other characters I have observed, there exists a wide difference in the properties of these two compounds, and a further study of them may lead to some new and interesting results.